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Wastes from Manufacture of Dyes and Pigments. Volume 3. Stilbene Dyes and Fluorescent Brightening Agents

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WASTES FROM MANUFACTURE OF DYES AND PIGMENTS: VOLUME 3. STILBENE DYES AND FLUORESCENT BRIGHTENING AGENTS

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The chemistry of these dyes and pigments is discussed as well as the overall production process and waste treatment practices. Several waste streams that could contain hazardous material are identified and five companies that produce representative dyes and pigments are recommended for a sampling program to confirm the composition and amounts of these waste streams.

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report is one of a series of preliminary studies of segments of the dye and pigment manufacturing industry conducted for the Organic and Inorganic Chemicals and Products Branch of the Industrial Pollution Control Division. The objective of these studies was to determine if process waste streams might contain hazardous material and to recommend sites where a sampling program could be used to confirm the nature of any hazards that were identified.

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ABSTRACT

A preliminary study of the manufacture of Stilbene dyes and fluorescent brightening agents was conducted to determine if process waste streams might contain hazardous material. The study first identifies the dyes and pigments that belong to this segment of the industry, the amounts produced and the known U.S. producers.

The chemistry of these dyes and pigments is discussed as well as the overall production process and waste treatment practices. Several waste streams that could contain hazardous material are identified and five companies that produce representative dyes and pigments are recommended for a sampling program to confirm the composition and amounts of these waste streams.

This report is submitted in fulfillment of contract No. 68-03-2944 by SRI International under the sponsorship of the U.S. Environmental Protection Agency. The report covers the period December 1981 to August 1982, and work was completed as of July 31, 1983.

CONTENTS

FOREWORD..... iii

ABSTRACT..... iv

TABLES..... vi

1. INTRODUCTION..... 1

2. SUMMARY AND CONCLUSIONS..... 6

3. PROCESS CHEMISTRY..... 7

Introduction..... 7
Stilbene Dyes..... 7
Fluorescent Brightening Agents..... 11

4. ORGANIC AND INORGANIC INTERMEDIATES AND REAGENTS USED IN THE PRODUCTON OF STILBENE DYES AND FLUORESCENT BRIGHTENING AGENTS..... 14

5. SOURCES OF WASTE DISCHARGES DURING DYE AND PIGMENT MANUFACTURING..... 16

Overview of Dye and Pigment Production Processes..... 16
Material in the Waste Streams from Stilbene Dyes and Fluorescent Brighteners Production..... 18

REFERENCES..... 25

TABLES

Number		Page
1.	Stilbene Dyes and Fluorescent Brightening Agents Included in This Study	3
2.	Stilbene Dyes and Fluorescent Brightening Agents of Known 1979 U.S. Commercial Production	5
3.	Inorganic Reagents Used to Produce Stilbene Dyes and Fluorescent Brightening Agents	14
4.	Organic Intermediates Used to Produce Stilbene Dyes and Fluorescent Brightening Agents	15
5.	Organic Materials that May Appear in the Waste Streams from the Production of Stilbene Dyes and Fluorescent Brighteners of Known Manufacturing Process	19
6.	Directory of Dye Manufacturers, 1979	22
7.	1979 Producers of Stilbene Dyes and Fluorescent Brightening Agents	23

SECTION 1

INTRODUCTION

The Resource Conservation and Recovery Act (RCRA) requires that hazardous solid wastes produced by manufacturing operations be identified and disposed in a manner that limits the release of hazardous materials to the environment. To date, many specific waste streams from manufacturing processes are listed in regulations as being hazardous because of their chemical composition. The objective of this study was to determine if wastes produced by the manufacture of dyes and pigments in the United States require listing as hazardous materials. An analysis of both the chemistry and the physical processing involved in dye and pigment manufacturing is used to identify all wastes that may contain significant chemical hazards. An analysis of the industry is used to determine specific manufacturers where the candidate wastes may be produced. This information allows contractors of the U.S. Environmental Protection Agency to design a sampling and analysis program to confirm or disprove the presence of hazardous materials in the candidate wastes and thereby develop a basis for listing dye and pigment manufacturing wastes under RCRA. This report deals with the wastes produced from the manufacture of stilbene dyes and fluorescent brightening agents.

The stilbene dyes share in common the structural constituent 2,2'-stilbene disulfonic acid. However, the stilbene dyes' chromophoric system is due to the presence of an azo or azoxy group. Even though the stilbene dyes are a subdivision of the azo class, they are treated as a separate class because they are not prepared by the classical azo coupling reaction (Bomberger and Boughton, 1983). Many fluorescent optical brighteners are also based on stilbene derivatives and these are included in the Colour Index (The Society of Dyers and Colourists, 1980) with the stilbene dyes.

According to the U.S. Tariff Commission (1974), the U.S. commercial production of stilbene dyes and brighteners for 1972 was 14,000 metric tons. This represented 12% of the total reported U.S. commercial dye production of 120,000 metric tons for that year. The stilbene dyes and fluorescent brightening agents represented the third largest structural class of dyes based on U.S. commercial production volume. Approximately two-thirds of the stilbene dyes and brighteners production was attributable to the fluorescent brightening agents. Data on U.S. production of dyes by structural class have not been reported since 1972; therefore, it was not possible to determine from public sources whether the relative importance and/or total production of stilbene dyes and brighteners has changed.

Table 1 gives available 1979 U.S. production data for the 26 commercially significant stilbene dyes and fluorescent brightening agents included in this study--dyes produced at greater than 2.3 metric tons. Table 1 is arranged according to the Colour Index (C.I.) number (Colour Index, The Society of Dyers and Colourists, 1980). These 1979 U.S. production levels correspond to those reported in the Organic Dyes and Pigments Data Base prepared by SRI International (Swett et al., 1983). For 5 of the stilbene dyes and 19 of the fluorescent brightening agents, the production is shown only as an amount greater than a minimum number. This is because public sources do not list production values for dyes and pigments produced by fewer than three manufacturers or by three or more where one or two dominate the market.

Six of the 26 dyes and brighteners listed in Table 1 have a known 1979 U.S. commercial production volume. These dyes are listed in Table 2, arranged according to their production volume. These six dyes represent a combined 1979 U.S. commercial production of 2,300 metric tons.

Production data are for commercial product, which may include solvents, other diluents, and impurities in addition to the specific dye chemical of interest. No information was found concerning the concentration of the chemical dye in the commercial product.

The six dyes and two brighteners listed in Table 1 with a C.I. number have known process chemistry. The remaining dyes and brighteners are of unknown structure and process chemistry. This information on these proprietary dyes and brighteners is not available through public sources. Therefore, in this study we discuss only the process chemistry and waste production of the stilbene dyes and brighteners of known process chemistry.

Table 1

STILBENE DYES AND FLUORESCENT BRIGHTENING AGENTS
INCLUDED IN THIS STUDY

C.I. No.	C.I. Name	1979 U.S. Commercial Production (metric tons/yr)
40000	Direct Yellow 11	1449.7
40001	Direct Yellow 6	147.4
40002 and 40003[a]	Direct Orange 15	204.6
40210	Direct Orange 61	>2.3
40215[b] 40220[c]	Direct Orange 34	>4.5
40215[b]	Direct Orange 39	83.5
40622	Fluorescent Brightener 28	273.5
40645	Fluorescent Brightener 46	>2.3
--	Direct Yellow 39	>2.3
--	Direct Yellow 103	>2.3
--	Direct Yellow 105	137.4
--	Direct Yellow 114	>2.3
--	Fluorescent Brightener 22	>2.3
--	Fluorescent Brightener 24	>2.3
--	Fluorescent Brightener 49	>2.3
--	Fluorescent Brightener 52	>2.3
--	Fluorescent Brightener 61	>9.1
--	Fluorescent Brightener 71	>2.3
--	Fluorescent Brightener 126	>2.3
--	Fluorescent Brightener 127	>2.3
--	Fluorescent Brightener 128	>2.3
--	Fluorescent Brightener 129	>2.3
--	Fluorescent Brightener 134	>2.3

Table 1 (Concluded)

C.I.No.	C.I. Name	1979 U.S. Commercial Production (metric tons/yr)
--	Fluorescent Brightener 148	> 2.3
--	Fluorescent Brightener 191	> 2.3
--	Fluorescent Brightener 200	> 2.3

[a]The stilbene dye C.I. Direct Orange 15 has two C.I. numbers associated with it: C.I. 40002 and C.I. 40003. The commercial products differ according to the reducing agents used in manufacture.

[b]The C.I. number 40215 has been assigned to the stilbene dyes C.I. Direct Orange 34, 39, 44, 46, and 60. These commercial products differ according to the proportion of reactants used and the aftertreatment.

[c]The stilbene dye C.I. Direct Orange 34 has two C.I. numbers associated with it: C.I. 40215 and C.I. 40220. The reactants used in manufacture differ.

CLASSIFICATION

Table 2

STILBENE DYES AND FLUORESCENT BRIGHTENING AGENTS
OF KNOWN 1979 U.S. COMMERCIAL PRODUCTION

C.I. No.	C.I. Name	1979 U.S. Commercial Production (metric tons/yr)
40000	Direct Yellow 11	1449.7
40622	Fluorescent Brightener 28	273.5
40002 and 40003[a]	Direct Orange 15	204.6
40001	Direct Yellow 6	147.4
--	Direct Yellow 105	137.4
40215	Direct Orange 39	83.5

[a]The stilbene dye C.I. Direct Orange 15 has two C.I. numbers associated with it: C.I. 40002 and C.I. 40003. The commercial products differ according to the reducing agents used in manufacture.

SECTION 2

SUMMARY AND CONCLUSIONS

In this preliminary study of the production of stilbene dyes and fluorescent brightening agents, several waste streams were identified that might contain hazardous materials:

- Discarded shipping containers. These would contain dye intermediates and reagents.
- Solid residues from process synthesis, distillation, and filtration. These would contain unreacted dye intermediates and reagents and reaction by-products.
- Gaseous emissions that may contain nitrogen oxides.
- Process wastewater that may contain mother liquor from filtering operations. This is probably the major source of discharge of organic chemicals from most plants.
- Wastewater treatment solids. The solids may be contaminated with low levels of all of the dye intermediates as well as the dyes themselves and some reaction by-products.

The information on the producers of dyes and pigments contained in Section 5 (Tables 5 and 7) along with the production volume information of Table 2 was analyzed to choose a few representative production facilities where a sampling program might be conducted to determine the composition of the waste emissions. The following companies are recommended:

American Color & Chemical Corp.

American Cyanamid Co.

Ciba-Geigy Corp.

Toms River Chemical Corp.

Mobay Chemical Corp., Dyestuff Division.

The five companies that are recommended for a sampling program should yield samples from facilities using different manufacturing and waste treatment practices. Since there is some overlap in the dyes and brightening agents they produce, the five-company sampling program increases the chances of identifying material in the waste streams from manufacturing the same dye or brightening agent that may be sensitive to plant practices.

SECTION 3

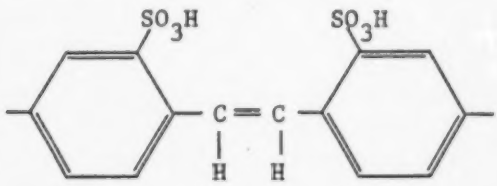
PROCESS CHEMISTRY

INTRODUCTION

A discussion of the production of stilbene dyes and fluorescent brightening agents is necessary to identify the emission sources and wastes that might be hazardous. This section focuses on the chemistry of the dye synthesis, with special attention given to the starting materials, intermediates, reaction conditions, and potential by-products.

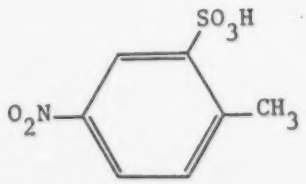
STILBENE DYES

The stilbene dyes form a small but important class of dyes. They are used extensively as direct dyes because of their excellent lightfastness, and attractive shade and because they are relatively inexpensive to manufacture. The stilbene dyes, which contain the structural constituent 2,2'-stilbene



disulfonic acid, are complex mixtures of substances that contain azo and azoxy groups as chromophores. The number and exact constitutional formulas of the individual components of the stilbene dyes are still unknown (Abrahart, 1977; Zweidler, 1969).

The principal starting material for production of stilbene dyes is 5-nitro-o-toluenesulfonic acid:



This intermediate is common to the manufacture of all stilbene dyes (Steadman et al., 1977; Zweidler, 1969).

Stilbene Dyes from 5-Nitro-o-toluenesulfonic Acid by Intermolecular Condensation

Yellow and orange dyes of good fastness to cotton are prepared by boiling 5-nitro-o-toluenesulfonic acid with dilute sodium hydroxide solution. Figure 1 shows the process chemistry route for three of the most important stilbene dyes that are manufactured via the self-condensation of 5-nitro-o-toluenesulfonic acid: C.I. Direct Yellow 11 (C.I. 40000), C.I. Direct Orange 15 (C.I. 40002 and C.I. 40003), and C.I. Direct Yellow 6 (C.I. 40001) (see Table 2 for production volumes). As shown in Figure 1, the first stage of the self-condensation is the formation of the disodium salt of 4,4'-dinitroso-2,2'-stilbenedisulfonic acid (Venkataraman, 1952). Further heating with aqueous sodium hydroxide, varying the alkali concentration, temperature, and time of reaction leads to various yellow dyes. C.I. Direct Yellow 11 (C.I. 40000), the largest produced stilbene dye, is said to be produced at 65° to 75°C (Steadman et al., 1977). Oxidative aftertreatment with sodium hypochlorite of the self-condensation products leads to greenish-yellow shades. Reductive aftertreatment under alkaline conditions yields orange to brown-orange shades (Zweidler, 1969). Using the organic reducing agents glucose or glycerol produces C.I. Direct Orange 15, (C.I. 40002), whereas using sodium sulfide produces C.I. Direct Orange 15 (C.I. 40003) (The Society of Dyers and Colourists, 1980).

In the self-condensation of 5-nitro-o-toluenesulfonic acid, it is possible to produce 4,4'-dinitro-2,2'-stilbenedisulfonic acid, an important intermediate in stilbene dyes and fluorescent stilbene brighteners production (Abrahart, 1977). According to Venkataraman (1952), 5-nitro-o-toluenesulfonic acid is heated with a 3% sodium hydroxide solution to a temperature of 50° to 55°C. Then a 5% sodium hypochlorite solution containing 5% sodium hydroxide is gradually added until a slight excess of chlorine remains. This solution is agitated at 50 to 55°C for a few hours, then the intermediate 4,4'-dinitro-2,2'-stilbenedisulfonic acid is salted out. Reductive aftertreatment with an alkaline solution of formaldehyde at 90° to 93°C yields C.I. Direct Yellow 6 (C.I. 40001), as shown in Figure 1.

Each of these dyes are complex mixtures of substances. Very little is known about the exact molecular structure of the components of these dyes. However, it is generally accepted that the main constituent of C.I. Direct Yellow 11 (C.I. 40000) is the compound known as Curcumine S:

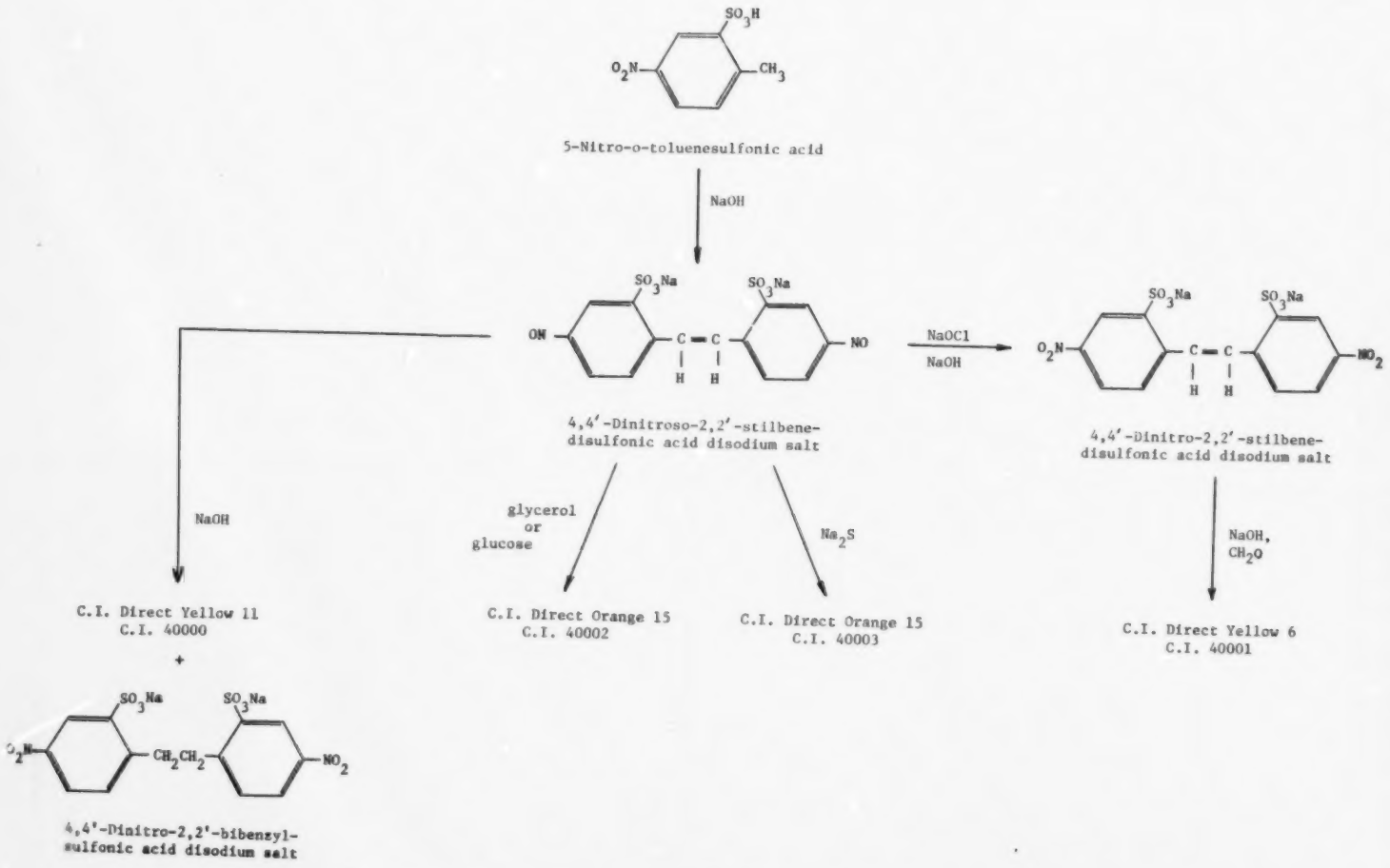
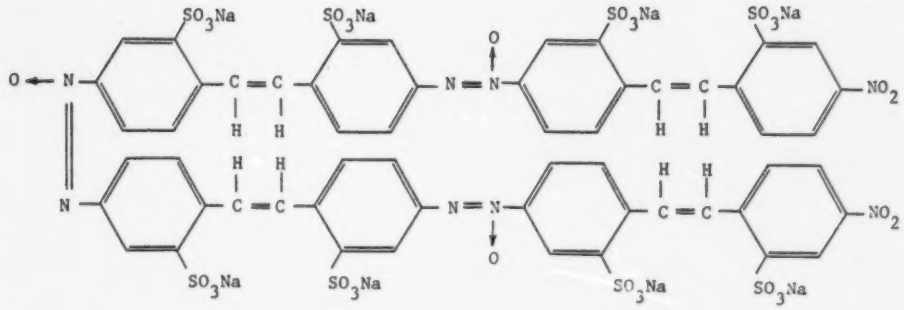


FIGURE 1 DYES FROM 5-NITRO-o- TOLUENESULFONIC ACID VIA INTERMOLECULAR CONDENSATION

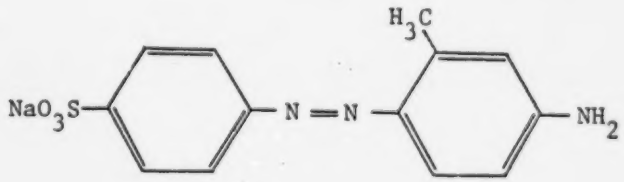


Curcumine S

Stilbene Dyes from Condensation of Amines with 4,4'-Dinitro-2,2'-stilbenedisulfonic Acid

A wide range of useful dyes can be made by condensing primary amines (e.g., aniline, p-phenylenediamine, benzidine, aminoazobenzene) with 4,4'-dinitro-2,2'-stilbenedisulfonic acid. The most important class of stilbene dyes produced by this route involves the condensation with aminoazo compounds, producing orange and scarlet shades. The product dyes are of the tetrakisazo type, but azoxy and other compounds are formed as by-products and part of the aminoazo compounds are consumed as reducing agent. The dyes formed are generally purified by an aftertreatment with hypochlorite, glucose, or sodium sulfide.

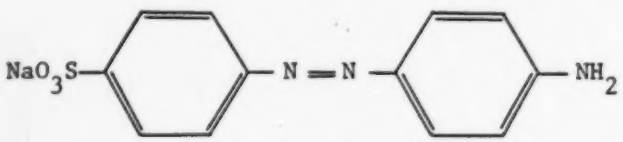
The stilbene dye, C.I. Direct Orange 34 (C.I. 40220), is prepared from the condensation of 4,4'-dinitro-2,2'-stilbenedisulfonic acid with the sodium salt of the monoazo compound (sulfanilic acid → m-toluidine*):



*It is the practice to describe monoazo dyes by the convention
amine → coupling component
in which the arrow indicates the appropriate primary aromatic amine has been diazotized and coupled to a coupling component.

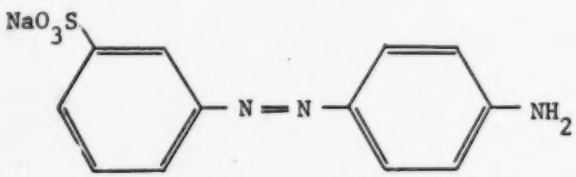
Typical conditions for this condensation are to mix 1 mole of 4,4'-dinitro-2,2'-stilbenedisulfonic acid with an equal weight of water, 1 mole of sodium hydroxide (as a 40% solution) and 1.75 moles of the aminoazo compound (Venkataraman, 1952). The mixture is agitated overnight, then the paste that forms is transferred to an autoclave and sodium hydroxide is added to form a 3.6% to a caustic soda solution. The mixture is then heated at 100°C for two to three hours. The dyestuff is precipitated by neutralizing excess alkali with hydrochloric acid and salting out.

Another form of C.I. Direct Orange 34 (C.I. 40215) is obtained by condensing 4,4'-dinitro-2,2'-stilbenedisulfonic acid with the sodium salt of the monoazo compound (sulfanilic acid → aniline) (C.I. 13010):



The manufacturing process is similar to that for C.I. 40220 except the resultant dye is aftertreated by reduction with glucose and sodium hydroxide solution. The properties of the dye are affected by the proportions of reactants and other process variables. In some cases quite different products are derived from the same components (Allen, 1971).

The dye C.I. Direct Orange 61 (C.I. 40210) is the condensation product of 4,4'-dinitro-2,2'-stilbenedisulfonic acid with the sodium salt of the monoazo compound (metanilic acid → aniline):



FLUORESCENT BRIGHTENING AGENTS

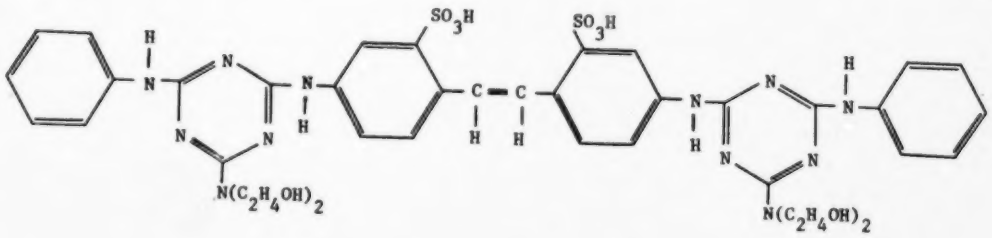
Fluorescent materials that are capable of absorbing radiation in the ultraviolet region between 330 and 380 nm and emitting light in the blue region of the visible spectrum between 430 and 490 nm are used extensively as optical brighteners in the textile and paper industries and in household detergents. The yellow appearance of a material (which is due to the absorption of blue-violet light) can be corrected by the emission of a corresponding amount of blue-violet light by the fluorescent compound. Fluorescent brightening agents have, in fact, largely replaced ultramarine and

other blueing agents that were formerly used to counteract the yellowness of textiles. (The application of a blue coloring matter causes absorption of yellow light, thereby making the yellowed fabric appear white. The real effect, however, is to extend the region of the spectrum over which light is absorbed so that the treated material appears pale grey rather than yellowish.)

For the molecules of the optical brighteners to possess high fluorescent activity and good cotton substantivity, the structural requirements of the brighteners are similar to a direct dye, apart from the presence of a chromophoric system: the molecule must possess a conjugated system, it must be planar, and it must contain electron-donating groups such as -OH and $-NH_2$ (Abrahart, 1971).

Fluorescent Brighteners from 4,4'-Diamino-2,2'-stilbenedisulfonic Acid

Most of the fluorescent brightening agents in use are from derivatives of 4,4'-diamino-2,2'-stilbenedisufonic acid (Abrahart, 1971; Zweidler, 1969). This intermediate is obtained by the Bechamp reduction (with iron) or catalytic reduction of 4,4'-dinitro-2,2'-stilbenedisulfonic acid. The largest group in this category, the bistriazinyl derivatives, are formed by reacting 4,4'-diamino-2,2'-stilbenedisulfonic acid with cyanuric chloride, followed by partial or total replacement of the reactive chlorine atoms with other groups. The fluorescent brightener with the largest known commercial production, C.I. Fluorescent Brightener 28 (C.I. 40622), is manufactured this way: 1 mole of 4,4'-diamino-2,2'-stilbenedisulfonic acid is condensed with 2 moles of cyanuric chloride and the resulting product reacted with 2 moles each of diethanolamine and aniline.

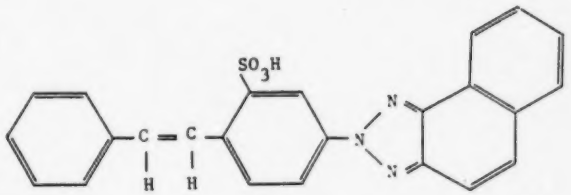


C.I. Fluorescent Brightener 28

C.I. 40622

Fluorescent Brighteners from 4-Aminostilbene

The class of mono(azol-2-yl)stilbenes arose from the efforts to find hypochlorite-stable products. The 2-(stilben-4-yl)-naphthotriazoles, represented by C.I. Fluorescent Brightener 46 (C.I. 40645), are prepared by diazotization of 4-amino-2-stilbenesulfonic acid, coupling with an ortho-coupling naphthalene derivative, and finally oxidizing to the triazole (Zweidler, 1978).



C.I. Fluorsecent Brightener 46

C.I. 40645

The coupling compound is 2-aminonaphthalene, and nitrous acid is the oxidizing agent used to form the triazole (The Society of Dyers and Colourists, 1980). According to Steadman et al. (1977), nitrogen oxides emissions might result from the manufacture of this brightener.

SECTION 4

ORGANIC AND INORGANIC INTERMEDIATES AND REAGENTS USED IN THE PRODUCTION OF STILBENE DYES AND FLUORESCENT BRIGHTENING AGENTS

Information on the organic and inorganic intermediates and reagents used to produce the stilbene dyes and fluorescent brightening agents listed in Table 1 was compiled from information in the Colour Index (The Society of Dyers and Colourists, 1980) and Steadman et al. (1977). These sources provided information on the process chemistry of six of the stilbene dyes and two of the fluorescent brightening agents listed in Table 1. The remaining four dyes and fourteen fluorescent brighteners have no assigned Colour Index number and are of unknown chemical structure. Their process information is proprietary and unavailable through public sources.

Table 3 lists the inorganic intermediates and Table 4 lists the organic reagents used in the production of the stilbene dyes and brighteners. Table 4 also identifies those substances which, if present in solid wastes, are subject to regulation as hazardous wastes under RCRA (Federal Register, 1980). Those substances are identified by their RCRA hazard code. None of the substances listed in Table 3 are identified as hazardous materials under RCRA.

Table 3

INORGANIC REAGENTS USED TO PRODUCE STILBENE DYES AND FLUORESCENT BRIGHTENING AGENTS

Hydrochloric acid
Iron
Sodium bisulfite
Sodium hydroxide
Sodium hypochlorite
Sodium nitrite
Sodium sulfide

Table 4

ORGANIC INTERMEDIATES USED TO PRODUCE
STILBENE DYES AND FLUORESCENT BRIGHTENING AGENTS

Organic Intermediate	Hazardous Waste Listing[a]
4-Aminoazobenzene (p-Phenylazoaniline)	
4-Amino-3′-azobenzenesulfonic acid, sodium salt	
4-Amino-4′-azobenzenesulfonic acid, sodium salt	
4-Amino-2-methyl-4′-azobenzenesulfonic acid, sodium salt	
m-Aminobenzenesulfonic acid (Metanilic acid; Meta-sulfanilic acid)	
m-Aminobenzenesulfonic acid, sodium salt (Sodium metanilate)	
p-Aminobenzenesulfonic acid (Sulfanilic acid)	
p-Aminobenzenesulfonic acid, sodium salt	
2-Aminonaphthalene (2-Naphthylamine)	T
2-Amino-1-naphthalenesulfonic acid	
4-Amino-2-stilbenesulfonic acid	
Aniline	I
Anilinomethanesulfonic acid	
Cyanuric chloride (Trichloro-s-triazine)	
4,4′-Diamino-2,2′-stilbenedisulfonic acid	
Diethanolamine (DEA; di(2-hydroxyethyl) amine)	
4,4′-Dinitro-2,2′-stilbenedisulfonic acid	
4,4′-Dinitro-2,2′-stilbenedisulfonic acid, disodium salt	
Formaldehyde	T
Glucose	
5-Nitro-o-toluenesulfonic acid	
1,2,3-Propanetriol (Glycerol)	
m-Toluidine (m-Aminotoluene)	

[a]Federal Register (1980), indicate the basis for EPA listing the material hazardous: Ignitable (I) and Toxic (T).

SECTION 5

SOURCES OF WASTE DISCHARGES DURING DYE AND PIGMENT MANUFACTURING

The wide range of dye and pigment production processes and the specific plant characteristics and process control capabilities make estimation of material losses during dye manufacture a difficult task. In general, the most significant material losses are intermediates that do not react and by-products such as incomplete dye or pigment molecules. The intermediates and by-products from dye manufacturing are present either in the product or in the solid waste streams regulated under RCRA, which include wastewater, solid residues, and the vapor and dust emissions. The material in the wastewater is discharged in the plant effluent and on wastewater treatment solids.

OVERVIEW OF DYE AND PIGMENT PRODUCTION PROCESSES

Figure 2 illustrates the dye and pigment manufacturing process and shows where the losses of materials occur. The dye manufacturing equipment required to produce stilbene dyes and fluorescent brighteners consists of stirred, batch reactors constructed of iron and fitted with a reflux condenser and standard filter presses, grinders, dryers, and blenders (Steadman et al., 1977).

The dyes or pigments are usually produced in batches, and the plants typically contain several reactor trains. Complex dyes may require use of several reactor trains. Production of colors is usually rotated by set schedules from light- to dark-colored dyes to minimize the impact of dye carry-over from multiple use of the equipment.

The sources of wastes from dye manufacture identified in Figure 2 are summarized below:

- Material handling--Air emissions from raw material dusting and volatilization, solid residues on shipping containers, and process wastewaters from equipment washdown.
- Dye syntheses--Air emissions from the volatilization of intermediates and by-products from reaction vessels, solid residues from distillation residues and spills, and process wastewaters from equipment washdown.
- Product and intermediate filtration--Air emissions from unreacted intermediate and by-product volatilization during material handling, solid residues from spills, and process wastewater from equipment

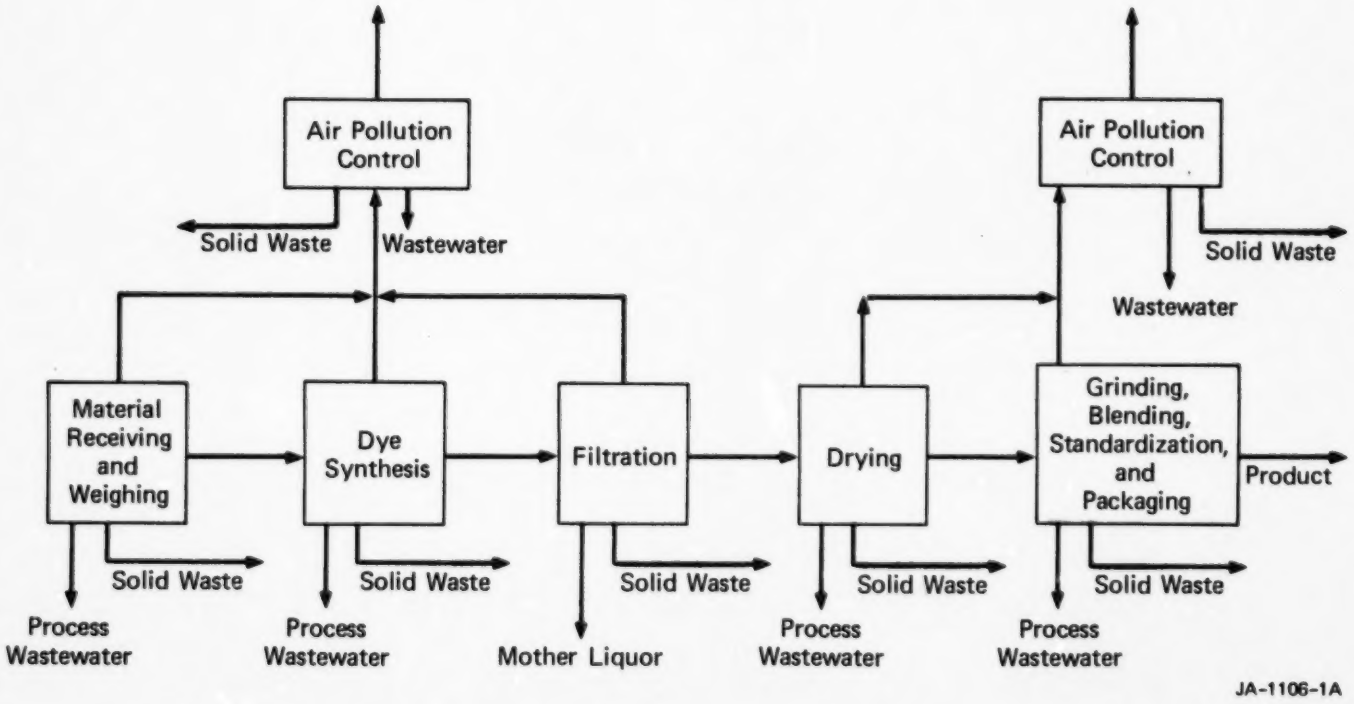


FIGURE 2 PRODUCTION OPERATIONS THAT ARE SOURCES OF WASTE EMISSIONS IN DYE AND PIGMENT MANUFACTURE

washdown. A significant additional source of process wastewater is the mother liquor.

- Drying--Air emissions from volatilization of by-products and unreacted intermediates in the drying oven, and solid residues from spills and dusting of the product dye.
- Grinding, blending, standardization, and packaging--Solid residues from dusts produced by the grinding operations that may be either in the air streams from vent systems designed to prevent the material from entering the workplace environment or in the solid residue from spills.
- Air pollution control--Solid residues from baghouses or scrubbers collecting fine dusts and process wastewater from scrubbers.

MATERIAL IN THE WASTE STREAMS FROM STILBENE DYES AND FLUORESCENT BRIGHTENERS PRODUCTION

Previous studies (Lapp et al., 1979; Bomberger and Boughton, 1983) have demonstrated that the major potential source of emissions is the process wastewater, primarily because it contains the mother liquor.

On the basis of the chemistry discussed in Section 3, these mother liquors, obtained from purifying the dyes, will probably contain unreacted intermediates, reaction by-products, unprecipitated dye or pigment, and salt.

Table 5 lists the stilbene dyes and fluorescent brighteners for which process chemistry information was available, identifying the intermediates and other organic chemicals used in the production and lists the producers of the stilbene dyes and fluorescent brighteners. Table 5 does not identify process chemistry by-products that are likely to be present, for example, isomers of required intermediates and the reaction product of these with the other intermediates and reagents used in the process. The by-products were not included in this study because very little useful information dealing with the amount or nature of these by-products was found.

Table 6 gives the full names of the producers associated with the letter codes in Table 5. The identity and corporate ownership of the producers is based on 1979 information. Since then, several dye production facilities or dye lines were sold. Sales that were announced in trade journals are shown as footnotes to Tables 7 and 9. A systematic search was not made to verify that all such sales have been listed, so the tables may not be complete. Table 7 lists all the producers of the stilbene dyes and fluorescent brightening agents listed in Table 1 and the dyes and brighteners each producer manufactured in 1979.

The most significant known hazardous waste components from the production of stilbene dyes and fluorescent brightening agents of known process chemistry are the aniline, formaldehyde, and 2-naphthylamine used in the manufacture of many of the stilbene derivatives. Steadman et al. (1977) also report that nitrogen oxides emissions might result from the manufacture of one of the stilbene brighteners, C.I. Fluorescent Brightener 46 (C.I. 40645).

Table 5

ORGANIC MATERIALS THAT MAY APPEAR IN THE WASTE STREAMS FROM THE PRODUCTION OF STILBENE DYES AND FLUORESCENT BRIGHTENERS OF KNOWN MANUFACTURING PROCESS

1979 U.S. Commercial Producers	C.I. No.	C.I. Name	1979 U.S. Commercial Production (metric tons/yr)	Materials Released to the Environment
AC,ACY BAS,DUP TRC,VPC	40000	Direct Yellow 11	1449.7	Direct Yellow 11 4,4'-Dinitro-2,2'-bibenzylsulfonic acid, disodium salt 5-Nitro-o-toluenesulfonic acid
ACY BAS DUP LVR	40001	Direct Yellow 6	147.4	Direct Yellow 6 4,4'-Dinitro-2,2'-stilbenedisulfonic acid Formaldehyde 5-Nitro-o-toluenesulfonic acid
AC ACY BAS DUP TRC	40002 and 40003[a]	Direct Orange 15	204.6	Direct Orange 15 4,4'-Dinitro-2,2'-stilbenedisulfonic acid Glucose 5-Nitro-o-toluenesulfonic acid 1,2,3-Propanetriol
TRC	40210	Direct Orange 61	> 2.3	Direct Orange 61 4-Amino-3'-azobenzenesulfonic acid 4-Amino-3'-azobenzenesulfonic acid, sodium salt m-Aminobenzenesulfonic acid m-Aminobenzenesulfonic acid, sodium salt Aniline 4,4'-Dinitro-2,2'-stilbenedisulfonic acid 4,4'-Dinitro-2,2'-stilbenedisulfonic acid, disodium salt 5-Nitro-o-toluenesulfonic acid

Table 5 (Continued)

1979 U.S. Commercial Producers	C.I. No.	C.I. Name	1979 U.S. Commercial Production (metric tons/yr)	Materials Released to the Environment
ATL DUP	40215[c] and 40220[b]	Direct Orange 34	> 4.5	Direct Orange 34 p-Aminoazobenzene 4-Amino-4'-azobenzenesulfonic acid, sodium salt p-Aminobenzenesulfonic acid p-Aminobenzenesulfonic acid, sodium salt 4-Amino-2-methyl-4'-azobenzenesulfonic acid, sodium salt Aniline 4,4'-Dinitro-2,2'-stilbenedisulfonic acid 4,4'-Dinitro-2,2'-stilbenedisulfonic acid, disodium salt Formaldehyde Glucose 5-Nitro-o-toluenesulfonic acid m-Toluidine
AC ACY CK FAB	40215[c]	Direct Orange 39	83.5	Direct Orange 39 p-Aminoazobenzene 4-Amino-4'-azobenzenesulfonic acid, sodium salt p-Aminobenzenesulfonic acid p-Aminobenzenesulfonic acid, sodium salt Aniline Anilinomethanesulfonic acid 4,4'-Dinitro-2,2'-stilbenedisulfonic acid 4,4'-Dinitro-2,2'-stilbenedisulfonic acid, disodium salt Formaldehyde Glucose 5-Nitro-o-toluenesulfonic acid

Table 5 (Concluded)

1979 U.S. Commercial Producers	C.I. No.	C.I. Name	1979 U.S. Commercial Production (metric tons/yr)	Materials Released to the Environment
CCW CGY VPC	40622	Fluorescent Brightener 28	273.5	Fluorescent Brightener 28 Aniline 4,4'-Dinitro-2,2'-stilbenedisulfonic acid Diethanolamine Cyanuric chloride 5-Nitro-o-toluenesulfonic acid
CGY	40645	Fluorescent Brightener 46	> 2.3	Fluorescent Brightener 46 2-Aminonaphthalene 2-Amino-1-naphthalenesulfonic acid 4-Amino-2-stilbenesulfonic acid

[a]The stilbene dye C.I. Direct Orange 15 has two C.I. numbers associated with it: C.I. 40002 and C.I. 40003. The commercial products differ according the reducing agents used in manufacture.

[b]The stilbene dye C.I. Direct Orange 34 has two C.I. numbers associated with it: C.I. 40215 and C.I. 40220. The reactants used in manufacture differ.

[c]The C.I. number 40215 has been assigned to the stilbene dyes C.I. Direct Orange 34 and 39. These commercial products differ according to the proportion of reactants used and the aftertreatment.

Table 6

DIRECTORY OF DYE MANUFACTURERS, 1979

Names of manufacturers that reported production and/or sales of stilbene dyes and fluorescent brightening agents to the U.S. International Trade Commission for 1979 are listed below in order of their identification codes as used in Table 5.

Code	Name of Company
AC	American Color & Chemical Corp.
ACY	American Cyanamid Co.
ATL	Atlantic Chemical Corp.
BAS	BASF Wyandotte Corp. & Pigments Div.
CCW	Cincinnati Milacron Chemicals, Inc.
CGY	Ciba-Geigy Corp.
CK	Crompton & Knowles Corp., Dyes & Chemical Div.
DGO	Day-Glo Color Corp.
DUP[a]	E. I. duPont de Nemours & Co., Inc.
FAB	Fabricolor Manufacturing Corp.
LVR	C. Lever Co., Inc.
S	Sandoz, Inc., Colors & Chemicals Div.
TRC	Toms River Chemical Corp.
VPC	Mobay Chemical Corp., Dyestuff Div.
X	Undesignated Manufacturer

[a] In 1979 duPont sold its paper dye operations to Mobay Chemical Corp., and its textile dye operations to Ciba-Geigy Corp. and Crompton and Knowles Corp. In 1979 duPont sold its dyes for ink operations to Morton Norwich Products Inc., Morton Chemical Co. Division.

Table 7

1979 PRODUCERS OF STILBENE DYES
AND FLUORESCENT BRIGHTENING AGENTS

C.I. No.	C.I. Name
American Color & Chemical Corp.	
40000	Direct Yellow 11
40002 and 40003[a]	Direct Orange 15
40215[b]	Direct Orange 39
—	Direct Yellow 105
American Cyanamid Co.	
40000	Direct Yellow 11
40001	Direct Yellow 6
40002 and 40003[a]	Direct Orange 15
40215[b]	Direct Orange 39
—	Direct Yellow 114
—	Fluorescent Brightener 61
Atlantic Chemical Corp.	
40215[a] and 40220[c]	Direct Orange 34
—	Direct Yellow 103
BASF Wyandotte Corp. & Pigments Div.	
40000	Direct Yellow 11
40001	Direct Yellow 6
40002 and 40003[a]	Direct Orange 15
—	Fluorescent Brightener 61
Cincinnati Milacron Chemicals, Inc.	
40622	Fluorescent Brightener 28
—	Fluorescent Brightener 61
Ciba-Geigy Corp.	
40622	Fluorescent Brightener 28
40645	Fluorescent Brightener 46
—	Fluorescent Brightener 22
—	Fluorescent Brightener 24
—	Fluorescent Brightener 71
—	Fluorescent Brightener 134
Crompton & Knowles Corp., Dyes & Chemical Div.	
40215[b]	Direct Orange 39
—	Direct Yellow 105
Day-Glo Color Corp.	
—	Fluorescent Brightener 61
E.I. du Pont de Nemours & Co., Inc.	
40000	Direct Yellow 11
40001	Direct Yellow 6
40002 and 40003[a]	Direct Orange 15
40215[b] and 40220[c]	Direct Orange 34

Table 7 (Concluded)

C.I. No.	C.I. Name
Fabricolor Manufacturing Corp.	
40215[b]	Direct Orange 39
C. Lever Co., Inc.	
40001	Direct Yellow 6
Sandoz, Inc., Colors & Chemicals Div.	
—	Fluorescent Brightener 49
—	Fluorescent Brightener 52
Toms River Chemical Corp.	
40000	Direct Yellow 11
40002 and 40003[a]	Direct Orange 15
40210	Direct Orange 61
—	Direct Yellow 39
—	Direct Yellow 105
Mobay Chemical Corp., Dyestuff Div.	
40000	Direct Yellow 11
40622	Fluorescent Brightener 28
—	Fluorescent Brightener 148
—	Fluorescent Brightener 191
—	Fluorescent Brightener 200
Undesignated Manufacturer[d]	
—	Fluroescent Brightener 126
—	Fluorescent Brightener 127
—	Fluorescent Brightener 128
—	Fluorescent Brightener 129

[a] The stilbene dye C.I. Direct Orange 15 has two C.I. numbers associated with it: C.I. 40002 and C.I. 40003. The commercial products differ according to the reducing agents used in manufacture.

[b] The C.I. number 40215 has been assigned to the stilbene dye C.I. Direct Orange 34, 39, 44, 46, and 60. These commercial products differ according to the proportion of reactants used and the aftertreatment.

[c] The stilbene dye C.I. Direct Orange 34 has two C.I. numbers associated with it: C.I. 40215 and C.I. 40220. The reactants used differ.

[d] According to the U.S. International Trade Commission (1980), the manufacturer(s) of Fluorescent Brighteners 126, 127, 128, and 129 did not consent to be identified with the designated product.

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